

α and β Relaxations of PMMA and Calculation of the Activation Energy



Summary

The use of DMA for the analysis of the α (T_g) and β relaxations of PMMA is shown in this application note. All relaxations are frequency dependent and the results of a multi-frequency experiment show clear events for both the α and the β relaxations. The activation energy of both relaxations is calculated using the Arrhenius equation.

Introduction

Dynamic Mechanical Analysis (DMA) is one of the most appropriate methods to investigate relaxation events. The glass transition (T_g) is a key process in any material and is sometimes referred to as the α transition. Normally at a lower temperature, other relaxation events can be observed for polymeric materials. The β relaxation is normally attributed to a polymer backbone conformation reorganization. The activation energy of these processes can be determined by performing an Arrhenius plot of the data. As frequency is essentially a rate expression with units of s^{-1} the natural log of frequency can be plotted against $1/T$. The slope of this line is equal to negative the activation energy divided by the gas constant.

DMA works by applying an oscillating force to the material and the resultant displacement of the sample is measured. From this, the stiffness can be determined and the modulus and $\tan \delta$ can be calculated. $\tan \delta$ is the ratio of the loss modulus to the storage modulus. By measuring the phase lag in the displacement compared to the applied force it is possible to determine the damping properties of the material. $\tan \delta$ is plotted against temperature and glass transition is normally observed as a peak since the material will absorb energy as it passes through the glass transition.

Experimental

Multi-frequency temperature scan of PMMA.

A bar of PMMA was clamped in the Single Cantilever Bending clamps and cooled with LN2 to -25 °C. The experiment collected data at all frequencies during the same experiment.

Equipment	Experimental Conditions
DMA 8000	
1L Dewar	Sample: PMMA
	Geometry: Single Cantilever Bending
	Dimensions: 7.3 (l) x 7.4 (w) x 2.0 (t) mm
	Temperature: -25 °C to 180 °C at 2 °C min ⁻¹
	Frequency: 0.1 to 10 Hz (5 discrete frequencies)

Results and conclusion

The raw tan δ data from the experiment is shown in Figure 1. Modulus data is not shown for the purposes of this application note. A clear glass transition is observed that has strong frequency dependence.

Figure 2 shows an expanded and enlarged section from -40 °C to 80 °C. As well as being expanded, a baseline subtraction was also applied. This is because the glass transition overlaps the β relaxation to a small degree. When the whole glass transition is subtracted from the data, the second graph on the right is produced. It is clear that a β relaxation is visible. Again, this is frequency dependant as expected for a relaxation event.

The Arrhenius equation can be expressed as RT

$$\ln(F) = \ln(A) = \frac{Ea}{RT}$$

where F is frequency, A is the preexponential factor, Ea is the activation energy, R is the gas constant and T is temperature. A plot of ln frequency against 1/temperature is known as an Arrhenius plot.

The Arrhenius plot with a line of best fit and the equation of that line is shown in Figure 3. The higher temperature glass transition data is shown in black and the lower temperature β relaxation is shown in red. The slope of each line is equal

to negative the activation energy divided by the gas constant. The activation energy for the β relaxation of PMMA is calculated to be 65 kJmol⁻¹ and for the glass transition is 368 kJmol⁻¹. Both lines show excellent fit parameters.

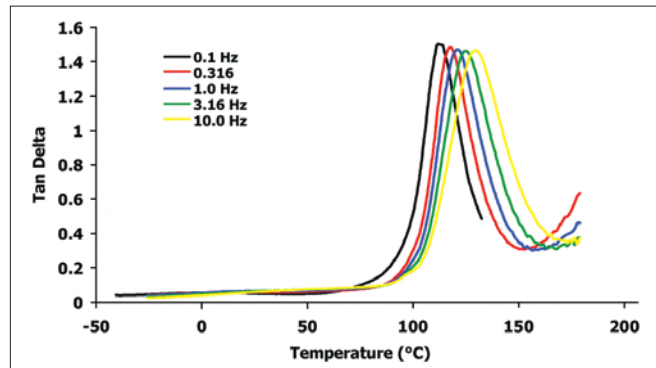


Figure 1. Raw tan δ from the experiment.

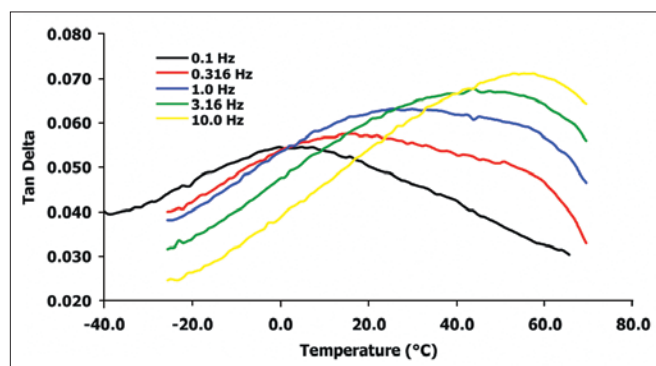


Figure 2. Raw tan δ from -40 °C to 80 °C.

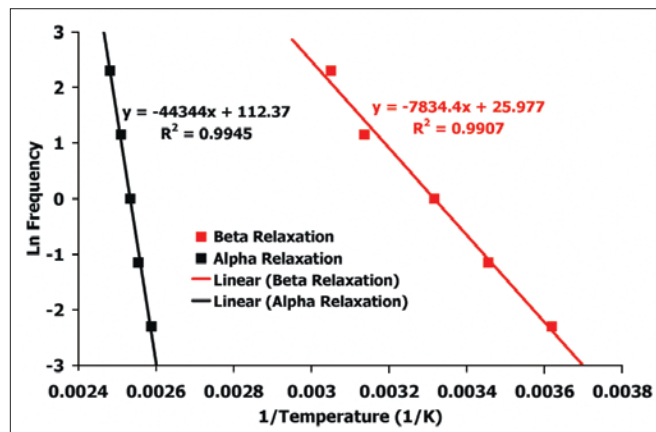


Figure 3. Arrhenius plot.